PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 0000054175	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP 03/14443	International filing date *(day/month/year)* 18.12.2003	Priority date *(day/month/year)* 20.12.2002
International Patent Classification (IPC) or both national classification and IPC A01N43/72		
Applicant BASF AKTIENGESELLSCHAFT et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 6 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand 18.06.2004	Date of completion of this report 14.02.2005
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Marie, G Telephone No. +49 89 2399-2571

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP 03/14443

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-78	as originally filed

Claims, Numbers

1 (part)	as originally filed
1 (part), 2-9	received on 21.09.2004 with letter of 20.09.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-9
	No:	Claims	-
Inventive step (IS)	Yes:	Claims	1-9
	No:	Claims	-
Industrial applicability (IA)	Yes:	Claims	1-9
	No:	Claims	-

2. Citations and explanations

see separate sheet

Re Item I

Basis of the report

The documents to which this report refers are numbered in their order of appearance in the international search report.

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

The subject-matter of the present invention concerns the use of dibenzo(hetero)azepine derivatives of formula (I) or the enantiomers or diastereoisomers, salts or esters thereof for combatting insects, arachnids or nematodes (claim 1). The invention further relates to a method for controlling insects, arachnids and nematodes using said compounds (claim 2) and to a method for protecting growing plants from attack or infestation by said pests using said compounds (claim 3).
Compounds per se (Formula I-A, I-B, I-C and I-D as defined in claims 4-8 respectively) and compositions comprising said compounds and an agronomically acceptable carrier (claim 9) are also claimed.

1. **Novelty (Article 33(2) PCT)**
   D1 discloses arthropodicidal carboxanilide derivatives which structure differs from present formula (I).
   Documents **D2-D5** disclose some dibenzo(hetero)azepine compounds and their use in pharmaceutical compositions. Their structure differs from the subject-matter of present claims 4-8.

   None of the cited documents disclose the compounds, uses and methods as defined in the present set of claims.
   Novelty of the subject-matter claimed can therefore be acknowledged.

2. **Inventive step (Article 33(3) PCT)**
   The difference between the molecules of the present invention as claimed and those disclosed in **D1**, which is considered to represent the closest prior art (see in particular compounds of *claim 1* with Q=Q-7 or Q-8), lies in the nature of the substituent on the 7-membered ring of the dibenzo(hetero)azepine and in the presence of an intracyclic double-bond, namely an amidine in the present

invention vs. a hydrazone/hydrazine in **D1**. The man skilled in the art does not have any indication in said document that changing the hydrazone/hydrazine to an amidine group could solve the problem posed.

Inventive step of the whole application as claimed can therefore be acknowledged.

3. **Industrial applicability (Article 33(4) PCT)**
The subject-matter of the application as claimed fulfills the requirements of said article.

rated, partially saturated or aromatic rings are unsubstituted or substituted with any combination of 1 to 4 groups selected from amino, C_1-C_6-alkyl, C_2-C_6-alkenyl, C_2-C_6-alkynyl, C_1-C_6-alkoxy, C_2-C_6-alkenyloxy, C_2-C_6-alkynyloxy, C_1-C_6-alkylthio, C_2-C_6-alkenylthio, C_2-C_6-alkynylthio, C_1-C_6-alkylamino, di(C_1-C_6-alkyl)amino, C_2-C_6-alkenylamino, C_2-C_6-alkynylamino, C_1-C_6-hydroxyalkyl, hydroxycarbonyl-C_1-C_4-alkyl, C_1-C_6-alkoxycarbonyl-C_1-C_4-alkyl, formyl-C_1-C_4-alkyl, formyl-C_1-C_4-alkoxy, C_1-C_6-alkylcarbonyl-C_1-C_4-alkoxy, C_3-C_6-cycloalkyl, which is bonded directly or via an oxygen, sulfur or C_1-C_6-alkyl linkage, and C_5-C_8-cycloalkenyl, wherein the carbon atoms in these aliphatic groups can be substituted by 1 to 4 groups selected from halogen, cyano, hydroxy and nitro; or

phenyl or benzyl which may be substituted by halogen, C_1-C_4-alkyl or C_1-C_4-haloalkyl; or

R^3 and R^4 together form the chains $-(CH_2)_2N^+(O^-)(CH_2)_2-$ or $-(CH_2)_3N^+(O^-)(CH_2)_2-$;

m is 0, 1, 2, 3 or 4;

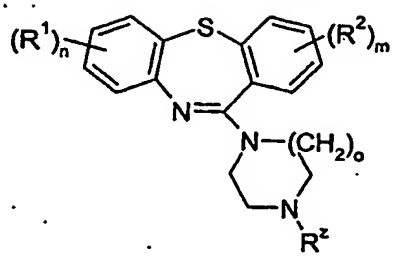
n is 0, 1, 2, 3 or 4;

or the enantiomers or diastereomers, salts or esters thereof for combatting insects, arachnids, or nematodes.

2. A method for controlling insects, arachnids or nematodes comprising contacting an insect, arachnid or nematode or their food supply, habitat or breeding grounds with a pesticidally effective amount of compounds of formula I as defined in claim 1 or compositions comprising them.

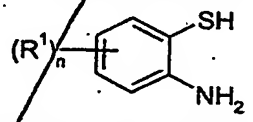
3. A method for protecting growing plants from attack or infestation by insects, arachnids or nematodes comprising contacting a plant, or soil or water in which the plant is growing, with a pesticidally effective amount of compounds of formula I as defined in claim 1 or compositions comprising them.

~~4. A process for the preparation of compounds of formula I A.~~



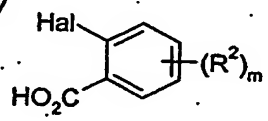
(I-A)

wherein R^z is hydrogen, amino, C_1-C_6-alkyl, C_2-C_6-alkenyl, C_2-C_6-alkynyl, C_1-C_6-alkoxy, C_2-C_6-alkenyloxy, C_2-C_6-alkynyloxy, C_1-C_6-hydroxyalkyl, hydroxycarbonyl-C_1-C_4-alkyl, C_1-C_6-alkoxycarbonyl-C_1-C_4-alkyl, formyl-C_1-C_4-alkyl, formyl-C_1-C_4-alkoxy, C_1-C_6-alkylcarbonyl-C_1-C_4-alkoxy, C_3-C_8-cycloalkyl, which is bonded directly or through an oxygen, sulfur or C_1-C_6-alkyl linkage, or C_5-C_8-cycloalkenyl, wherein the carbon atoms in these aliphatic groups can be substituted by 1 to 4 groups selected from halogen, cyano, hydroxy and nitro; or phenyl or benzyl which may be substituted by halogen, C_1-C_4-alkyl or C_1-C_4-haloalkyl; and wherein the group [N-R^z] may be present as amine oxide [$N^+(O^-)$-R^z]; o is 1 or 2, and the further variables and the indices are as defined for formula I in claim 1, wherein in a first step o-amino-thiophenol derivatives of formula II



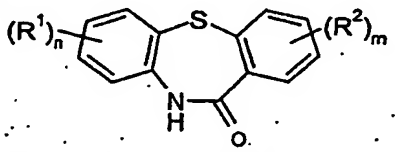
(II)

wherein R^1 and n are as defined for formula I in claim 1 are reacted with benzoic acid derivates III



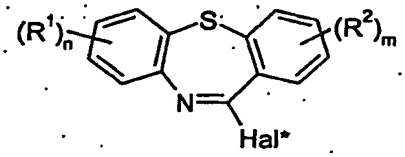
(III)

wherein Hal is halogen and R^2 and m are as defined for formula I in claim 1 in the presence of a base and a transition metal (I) oxide or - halogenid as catalyst to give compounds IV,



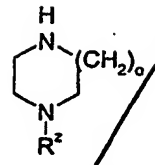
(IV)

which compounds are further reacted with a halogenating agent to yield compounds of formula V



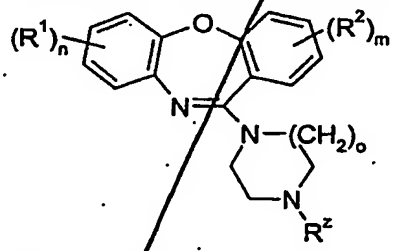
(V)

wherein Hal* is halogen which after reaction with piperazine derivates VI

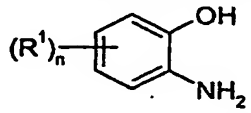

(VI)

wherein o and R^z are as defined for formula I-A give compounds I-A.

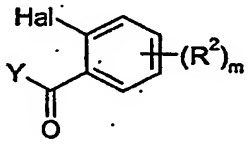
5. A process for the preparation of compounds of formula I-B


(I-B)

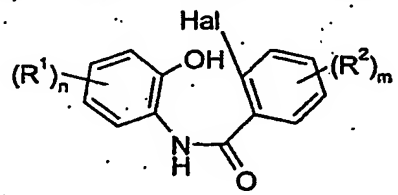
wherein the variables and the indices are as defined for formula I-A in claim 5. wherein in a first step o-amino-phenol derivatives of formula VII


(VII)

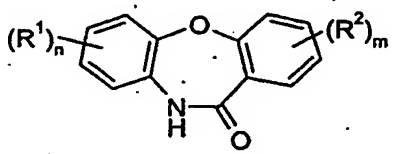
wherein R^1 and n are as defined for formula I in claim 1 are reacted with benzoic acid derivates III*


(III*)

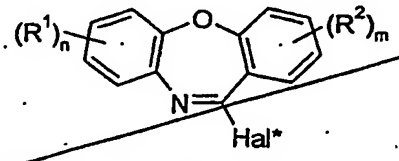
wherein Hal is halogen, Y is hydroxy, halogen or C_1-C_6-alkoxy and R^2 and m are as defined for formula I in claim 1 to give compounds VIII,


(VIII)

which in a second step are cyclizized in the presence of a base to give compounds IX


(IX)

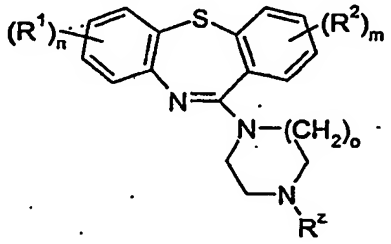
~~which compounds are further reacted with a halogenating agent to yield compounds of formula X~~



(X)

~~wherein the variables and the indices have the meanings as defined for formula I and Hal* is halogen which after reaction with piperazine derivates VI as defined in claim 5 give compounds I-B.~~

4 β. Compounds of formula I-A



(I-A)

wherein

R^1,R^2 are each independently halogen, hydroxy, mercapto, amino, cyano, nitro, C_1-C_6-alkyl, C_1-C_6-alkoxy, C_1-C_6-alkylamino, di(C_1-C_6-alkyl)amino, C_1-C_8-alkylthio, C_2-C_6-alkenyl, C_2-C_6-alkenyloxy, C_2-C_6-alkenylamino, C_2-C_6-alkenylthio, C_2-C_6-alkynyl, C_2-C_6-alkynyloxy, C_2-C_6-alkynylamino, C_2-C_6-alkynylthio, C_1-C_6-alkylsulfonyl, C_2-C_6-alkenylsulfonyl, formyl, or C_1-C_6-alkylcarbonyl, wherein the carbon atoms in the aliphatic and aromatic groups may be substituted by 1 to 3 groups selected from halogen, cyano, nitro, hydroxy, mercapto, amino, C_1-C_6-alkyl, C_1-C_6-alkoxy, C_2-C_6-alkenyloxy, C_2-C_6-alkynyloxy, C_1-C_6-haloalkoxy, or C_1-C_6-alkylthio;

R^z is hydrogen, C_1-C_6-alkyl, C_2-C_6-alkenyl, C_2-C_6-alkynyl, C_1-C_6-hydroxyalkyl, C_3-C_6-cycloalkyl, C_3-C_6-cycloalkyl-C_1-C_6-alkyl, or C_5-C_8-cycloalkenyl, wherein the carbon atoms in these aliphatic groups can be substituted by 1 to 4 groups selected from halogen, cyano, hydroxy and nitro; and wherein the group [N-R^z] may be present as amine oxide [$N^+(O^-)$-R^z];

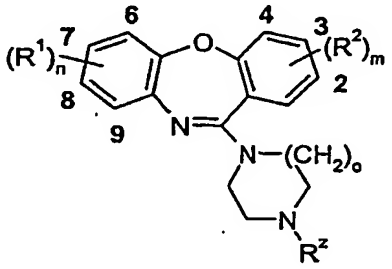
m is 1, 2, 3, or 4;

n is 1, 2, 3, or 4; and

o is 1 or 2.

5 7. Compounds of formula I-A according to claim 4 wherein R^1 and R^2 each independently are halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, methoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkylthio, C_1-C_6-haloalkylthio, C_2-C_6-alkenylthio, or C_2-C_6-alkynylthio.

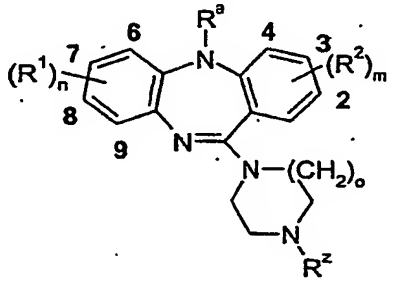
5 6 8. Compounds of formula I-B



(I-B)

wherein R^z and the indices n, m, and o are as defined for formula I-A in claim 6 and R^1 and R^2 each independently are halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, methoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkylthio, C_1-C_6-haloalkylthio, C_2-C_6-alkenylthio, or C_2-C_6-alkynylthio, with the proviso that
when R^1 is 2-chloro then R^2 is not 8-chloro or 8-methoxy; and
when R^1 is 4-chloro then R^2 is not 8-chloro; and
when R^1 is 4-methyl then R^2 is not 7-, 8-, or 9-chloro.

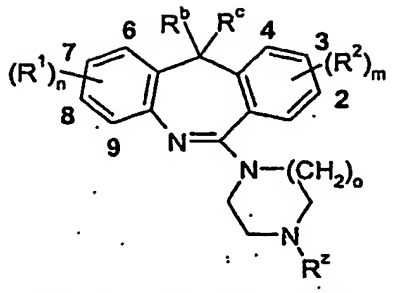
7 9. Compounds of formula I-C



(I-C)

wherein R^a is hydrogen or C_1-C_6-alkyl and the further variables and indices are as defined for formula I-B in claim 8, with the proviso that
not both of R^1 or R^2 are halogen and
when R^1 is 2-chloro then R^2 is not 8-methyl, 8-methylthio, or 8-methoxy; and
when R^1 is 2-methoxy, then R^2 is not 8-chloro; and
when R^1 is 2-methyl then R^2 is not 8-chloro.

8 10. Compounds of formula I-D



(I-D)

wherein R^b and R^c are each independently hydrogen, methyl or CR^bR^c represents $C=CH_2$, and the further variables and the indices are as defined for formula I-B in claim 8.

11. Compositions comprising compounds of formula I-A, I-B, I-C, and/or I-D as defined in claims 4 to 9 or the enantiomers or diastereomers, salts or esters thereof and an agronomically acceptable carrier.